

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 915 373 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

12.05.1999 Bulletin 1999/19

(51) Int. Cl.⁶: **G03C 1/76**, G03C 11/08

(21) Application number: **98203595.8**

(22) Date of filing: **26.10.1998**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **06.11.1997 US 965335**

(71) Applicant: **EASTMAN KODAK COMPANY
Rochester, New York 14650 (US)**

(72) Inventors:

• **Yau, Hwei-ling
Rochester, New York 14650-2201 (US)**

• **Krzemien, Wendy Susan**

Rochester, New York 14650-2201 (US)

• **Lubberts, Paul Thomas**

Rochester, New York 14650-2201 (US)

(74) Representative:

Parent, Yves et al

KODAK INDUSTRIE,

Département Brevets,

CRT - Zone Industrielle

71102 Chalon-sur-Saône Cedex (FR)

(54) **A novel protecting layer for gelatin based AGX photographic products**

(57) The present invention is an imaged photographic element which includes a support, at least one silver halide light-sensitive emulsion layer superposed on the support; and a protective overcoat furthest from the support. The protective overcoat is superposed on the silver halide light sensitive layer. the protective overcoat includes a first polymeric particle having a glass transition temperature of greater than or equal to 25 °C and a particle size of from 5 to 500 nm and a second polymeric particle having a glass transition temperature of less than 25 °C and a particle size of from 5 to 500 nm at a weight ratio of the first polymeric particle to the second polymeric particle of from 3:97 to 80:20 and wax particle having a size of from 0.01 µm to 0.5 µm. The protective overcoat is applied from an aqueous coating.

EP 0 915 373 A1

Description

CROSS REFERENCE TO RELATED APPLICATIONS

- 5 [0001] This application relates to commonly assigned copending application Serial No. 08/965,508, filed simultaneously herewith and hereby incorporated by reference for all that it discloses.

BACKGROUND OF THE INVENTION

- 10 [0002] Silver halide photographic elements contain light sensitive silver halide in a hydrophilic emulsion. An image is formed in the element by exposing the silver halide to light, or to other actinic radiation, and developing the exposed silver halide to reduce it to elemental silver.
- [0003] In color photographic elements a dye image is formed as a consequence of silver halide development by one of several different processes. The most common is to allow a by-product of silver halide development, oxidized silver
- 15 halide developing agent, to react with a dye forming compound called a coupler. The silver and unreacted silver halide are then removed from the photographic element, leaving a dye image.
- [0004] In either case, formation of the image commonly involves liquid processing with aqueous solutions that must penetrate the surface of the element to come into contact with silver halide and coupler. Thus, gelatin, and similar natural or synthetic hydrophilic polymers, have proven to be the binders of choice for silver halide photographic elements.
- 20 Unfortunately, when gelatin, and similar polymers, are formulated so as to facilitate contact between the silver halide crystal and aqueous processing solutions, they are not as tough and mar-resistant as would be desired for something that is handled in the way that an imaged photographic element may be handled. Thus, the imaged element can be easily marked by fingerprints, it can be scratched or torn and it can swell or otherwise deform when it is contacted with liquids.
- 25 [0005] There have been attempts over the years to provide protective layers for gelatin based photographic systems that will protect the images from damage by water or aqueous solutions. US Patent No. 2,173,480 describes a method of applying a colloidal suspension to moist film as the last step of photographic processing before drying. A series of patents describes methods of solvent coating a protective layer on the image after photographic processing is completed and are described in US Patent Nos. 2,259,009, 2,331,746, 2,798,004, 3,113,867, 3,190,197, 3,415,670 and
- 30 3,733,293. The application of UV-polymerizable monomers and oligomers on processed image followed by radiation exposure to form crosslinked protective layer is described US Patent Nos. 4,092,173, 4,171,979, 4,333,998 and 4,426,431. Major drawbacks for the solvent coating method and the radiation cure method are the health and environmental concern of those chemicals to the coating operator and the instability and relatively short shelf life of the coating solutions. US Patent Nos. 3,397,980, 3,697,277 and 4,999,266 describe methods of laminating polymeric sheet film on
- 35 the processed image as the protective layer. US Patent No. 5,447,832 describes the use of a protective layer containing mixture of high and low Tg latices as the water-resistance layer to preserve the antistat property of the V₂O₅ layer through photographic processing. This protective layer is not applicable to the image formation layers since it will detrimentally inhibit the photographic processing. US Patent No. 2,706,686 describes a lacquer finish for photographic emulsions, with the aim of providing water- and fingerprint-resistance by coating the emulsion, prior to exposure, with
- 40 a porous layer that has a high degree of water permeability to the processing solutions. After processing, the lacquer layer is fused and coalesced into a continuous, impervious coating. The porous layer is achieved by coating a mixture of a lacquer and a solid removable extender (ammonium carbonate), and removing the extender by sublimation or dissolution during processing. The overcoat as described is coated as a suspension in an organic solvent, and thus is not compatible with current manufacturing of photographic products. US Patent No. 3,443,946 provides a roughened
- 45 (matte) scratch-protective layer, but not a water-impermeable one. US Patent No. 3,502,501 provides protection against mechanical damage only; the layer in question contains a majority of hydrophilic polymeric materials, and must be permeable to water in order to maintain processability. US Patent No. 5,179,147 likewise provides a layer that is not water-protective.
- [0006] In USSN 08/698,838 a protective overcoat is formed by applying a coating, in the presence of a electric field, charged, clear polymeric particles to an imaged silver halide element so as to cause the particles to adhere to a surface
- 50 of the imaged element and then fusing the polymeric particles. In USSN 08/898,985 a protective overcoat is formed by applying a coating of hydrophobic polymer particles having an average size of 0.01 to 1 microns, a melting temperature of from 55 to 200 °C at a weight percent of 30 to 95, and gelatin at a weight percent of 5 to 70 over a silver halide light-sensitive emulsion layer. The silver halide light sensitive emulsion layer is developed to provide an imaged photographic
- 55 element. The hydrophobic polymer particles are then fused to form a protective overcoat. However, there remains a need to provide protective overcoats on photographic elements without a fusing step.
- [0007] Thus, there is a need to control the coefficient of friction of the overcoat layer in order to be run through photofinishing equipment and/or handled by the end-users properly. In addition, the desire to enhance the resistance of the

protective layer to scratches and to prevent prints from adhering to on another in high temperature and/or high humidity is still greatly recognized.

[0008] The temperature and residence time of photographic coating in the drying section of photofinishing equipment in the trade vary from 50 °C to 70 °C and from 30 seconds to 2.5 minutes. The actual temperature of gelatin coating during drying is much lower than the temperature set for the dryer due to the evaporation of water. In addition, it is necessary to be free of volatile organic compound (VOC) in the formulation to be user and environmental friendly. Under these stringent requirements, it appears that an aqueous colloidal dispersion of a Water insoluble polymeric material is an appropriate system for this technology. Water soluble materials will not provide any water resistance property.

[0009] US Patent No. 2,719,791 describes the use of an aqueous dispersion of organic plastic material, which yields a water and vapor permeable coating on drying. However, it is known that when dispersions of low Tg material ($T_g < 25$ °C) are used to obtain a water resistance protective coating, the surface of the protective coating has an undesirable tacky characteristic, which generally degrades other physical properties, such as print blocking, fingerprinting, dust attraction and high scratch propensity. When dispersions of high Tg materials ($T_g > 25$ °C) are used, it is not possible to form a continuous water resistance layer on the prints under the drying condition described above. US Patent No. 2,751,315 also describes the use of an aqueous dispersion of copolymer materials. It was recognized in this patent that low Tg materials were not suitable and therefore higher Tg polymers in combination with an organic solvent were used in order to form a water-resistant protective coating. The organic solvent that is released from the formulation during drying creates an environmental concern if used in the current photofinishing laboratories. US Patent No. 2,956,877 describes a method of applying a solution to a photographic image that solubilizes the processing reagents from the photographic products as well as forming a protective coating on its surface. The acid groups on the polymer degrades the water resistant property of the final protective layer, and the organic solvent required in the formulation is not suitable for high volume photofinishing laboratories.

[0010] There remains a need for an aqueous coatable, water-resistant protective coating that can be easily coated on imaged processed photographic products and dried into a continuous coating under drying conditions typical of photographic processing equipment while not releasing volatile organic compounds and while also providing a low coefficient of friction, improved resistance to scratching and high-temperature blocking, without any adverse effect on the gloss of the photographic product.

SUMMARY OF THE INVENTION

[0011] The present invention is an imaged photographic element which includes a support, at least one silver halide light-sensitive emulsion layer superposed on the support; and a protective overcoat furthest from the support. The protective overcoat is superposed on the silver halide light sensitive layer. the protective overcoat includes a first polymeric particle having a glass transition temperature of greater than or equal to 25 °C and a particles size of from 5 to 500 nm and a second polymeric particle having a glass transition temperature of less than 25 °C and a particle size of from 5 to 500 nm at a weight ratio of the first polymeric particle to the second polymeric particle of from 3:97 to 80:20 and wax particle having a size of from 0.01 μm to 0.5 μm . The protective overcoat is applied from an aqueous coating.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The present invention describes a volatile organic-solvent-free material formulation that is applied to a photographic product at the end of photographic processing and dried to form a water resistant, scratch resistant, fingerprint resistant durable overcoat. The material composition of this invention is a combination of two colloidal dispersions of water insoluble hydrophobic polymeric materials and wax particles. At least one of the polymeric materials has glass transition temperature equal to or higher than 25 °C to provide toughness and non-tacky surface properties. The second polymeric material has glass transition temperature below 25 °C in order to form a continuous film layer at the mild drying condition, such as used in typical photographic processing equipment. The weight ratio of the two polymeric materials is from 3:97 to 80:20 by weight. The average particle size of colloidal dispersions of polymeric materials is from 5 nm to 500 nm. The types of wax particles include dispersions of submicron size, from 0.01 μm to 0.5 μm wax particles such as offered commercially as aqueous dispersions of polyolefins, polypropylene, polyethylene, high density polyethylene, oxidized polyethylene, ethylene acrylic acid copolymers, microcrystalline wax, paraffin, and natural waxes. The preferred particle size for the wax particles is between 0.01 μm and 0.2 μm . The preferred amount used in the formulation is 1% to 30% by weight based on the total dry laydown of the protective overcoat formulation. The preferred melting temperature for the wax particles is higher than 60 °C. The protective layer formulation with the wax particles has lower friction coefficient, improved scratch resistance and lower propensity of blocking (prints adhering face to face) in high temperature environment. The dry laydown of the total materials on the surface of photographic product is from 0.3 g/m² to 6 g/m². Other components commonly used in photographic processing solutions, such as biocides, spreading aids (surfactants), and lubricants can also be incorporated in the formulation as needed. The concentration

of the formulation can be from 1% solids to 50% solids depending on the desired thickness of the protective layer, the machine speed, the dryer efficiency and other factors that may affect the application to the photographic product.

[0013] The colloidal dispersions of hydrophobic polymers used for the first or second polymeric particle in the present invention are generally latexes or hydrophobic polymers of any composition that can be stabilized in an water-based medium. Such hydrophobic polymers are generally classified as either condensation polymers or addition polymers. Condensation polymers include, for example, polyesters, polyamides, polyurethanes, polyureas, polyethers, polycarbonates, polyacid anhydrides, and polymers comprising combinations of the above-mentioned types. Addition polymers are polymers formed from polymerization of vinyl-type monomers including, for example, allyl compounds, vinyl ethers, vinyl esters, vinyl heterocyclic compounds, styrenes, olefins and halogenated olefins, unsaturated acids and esters derived from them, unsaturated nitriles, vinyl alcohols, acrylamides and methacrylamides, vinyl ketones, multi-functional monomers, or copolymers formed from various combinations of these monomers. Such latex polymers can be prepared in aqueous media using well-known free-radical emulsion polymerization methods and may consist of homopolymers made from one type of the above-mentioned monomers or copolymers made from more than one type of the above-mentioned monomers. Polymers comprising monomers which form water-insoluble homopolymers are preferred, as are copolymers of such monomers. Preferred polymers may also comprise monomers which give water-soluble homopolymers, if the overall polymer composition is sufficiently water-insoluble to form a latex. The aqueous phase of the latex or colloidal dispersion of the invention may contain water-soluble polymers in order to control, for example, the viscosity and flow characteristics. The aqueous phase may also include surfactants of the cationic, anionic, zwitterionic or non-ionic types. Further listings of suitable monomers for addition type polymers are found in US Patent No. 5,594,047 incorporated herein by reference.

[0014] This present invention uses wax particles in addition to two latex dispersions to improve the physical properties of the protective layer, such as reducing the coefficient of friction, improving scratch resistance and minimizing blocking propensity in high temperature environment without adversely affecting the gloss appearance of the photographic prints.

[0015] The photographic products according to the present invention have the unique features of water resistance, improved scratch resistance and improved thermal blocking performance. In addition, volatile organic solvents or compounds are not released from the formulation.

[0016] The imaged photographic elements protected in accordance with this invention are derived from silver halide photographic elements that can be black and white elements (for example, those which yield a silver image or those which yield a neutral tone image from a mixture of dye forming couplers), single color elements or multicolor elements. Multicolor elements typically contain dye image-forming units sensitive to each of the three primary regions of the spectrum. The imaged elements can be imaged elements which are viewed by transmission, such as negative film images, reversal film images and motion picture prints or they can be imaged elements that are viewed by reflection, such as paper prints. Because of the amount of handling that can occur with paper prints and motion picture prints, they are preferred imaged photographic elements for use in this invention.

[0017] The photographic elements in which the images to be protected are formed can have the structures and components shown in Research Disclosure 37038. Specific photographic elements can be those shown on pages 96-98 of Research Disclosure 37038 as Color Paper Elements 1 and 2. A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like. All of these can be coated on a support which can be transparent (for example, a film support) or reflective (for example, a paper support). Photographic elements protected in accordance with the present invention may also include a magnetic recording material as described in Research Disclosure, Item 34390, November 1992, or a transparent magnetic recording layer such as a layer containing magnetic particles on the underside of a transparent support as described in US 4,279,945 and US 4,302,523.

[0018] Suitable silver halide emulsions and their preparation, as well as methods of chemical and spectral sensitization, are described in Sections I through V of Research Disclosure 37038. Color materials and development modifiers are described in Sections V through XX of Research Disclosure 37038. Vehicles are described in Section II of Research Disclosure 37038, and various additives such as brighteners, antifoggants, stabilizers, light absorbing and scattering materials, hardeners, coating aids, plasticizers, lubricants and matting agents are described in Sections VI through X and XI through XIV of Research Disclosure 37038. Processing methods and agents are described in Sections XIX and XX of Research Disclosure 37038, and methods of exposure are described in Section XVI of Research Disclosure 37038.

[0019] Photographic elements typically provide the silver halide in the form of an emulsion. Photographic emulsions generally include a vehicle for coating the emulsion as a layer of a photographic element. Useful vehicles include both

naturally occurring substances such as proteins, protein derivatives, cellulose derivatives (e.g., cellulose esters), gelatin (e.g., alkali-treated gelatin such as cattle bone or hide gelatin, or acid treated gelatin such as pigskin gelatin), gelatin derivatives (e.g., acetylated gelatin, phthalated gelatin, and the like). Also useful as vehicles or vehicle extenders are hydrophilic water-permeable colloids. These include synthetic polymeric peptizers, carriers, and/or binders such as poly(vinyl alcohol), poly(vinyl lactams), acrylamide polymers, polyvinyl acetals, polymers of alkyl and sulfoalkyl acrylates and methacrylates, hydrolyzed polyvinyl acetates, polyamides, polyvinyl pyridine, methacrylamide copolymers, and the like.

[0020] Photographic elements can be imagewise exposed using a variety of techniques. Typically exposure is to light in the visible region of the spectrum, and typically is of a live image through a lens. Exposure can also be to a stored image (such as a computer stored image) by means of light emitting devices (such as LEDs, CRTs, etc.).

[0021] Images can be developed in photographic elements in any of a number of well known photographic processes utilizing any of a number of well known processing compositions, described, for example, in T.H. James, editor, The Theory of the Photographic Process, 4th Edition, Macmillan, New York, 1977. In the case of processing a color negative element, the element is treated with a color developer (that is one which will form the colored image dyes with the color couplers), and then with an oxidizer and a solvent to remove silver and silver halide. In the case of processing a color reversal element, the element is first treated with a black and white developer (that is, a developer which does not form colored dyes with the coupler compounds) followed by a treatment to render developable unexposed silver halide (usually chemical or light fogging), followed by treatment with a color developer. Development is followed by bleach-fixing, to remove silver or silver halide, washing and drying.

[0022] The present invention is illustrated by the following examples.

Examples

Material preparation:

[0023] Commercially available materials were dialyzed against distilled water for 16 hours using membrane with molecular weight cutoff of 20,000 to remove organic solvent and excess surfactants and salts.

Glass Transition Temperature (T_g) and Melting temperature (T_m)

[0024] Both glass transition temperature (T_g) and melting temperature (T_m) of the dry polymer material were determined by differential scanning calorimetry (DSC), using a ramping rate of 20 °C/minute. T_g is defined herein as the inflection point of the glass transition. T_m is defined herein as the peak of the melting transition. The glass transition temperatures and melting temperature of materials used in this invention are listed in Table 1 and Table 2.

Table 1

ID	Name	Source	Material Class	T _g (°C)
P1	AVI*	Kodak	Vinylidene chloride copolymer	46
P2	Joncryl ECO2189	SC Johnson	Acrylic emulsion polymer	98
P3	Joncryl ECO2177	SC Johnson	Acrylic emulsion polymer	21
P4	Witcobond W-234	Witco	Polyurethane	-39

* AVI is a terpolymer latex made by conventional emulsion polymerization method, consisting of acrylonitrile, vinylidene chloride and acrylic acid at the weight ratio of 15:79:6.

Particle size measurement

[0025] The average particle size of wax particle dispersion was measured by photon correlation spectroscopy. The results are shown in Table 2.

Table 2

ID	Name	Source	Material Class	Particle size (nm)	T _m (°C)
W1	Jonwax 26	S.C. Johnson	high density polyethylene	50	131

EP 0 915 373 A1

Table 2 (continued)

ID	Name	Source	Material Class	Particle size (nm)	Tm (°C)
W2	ME39235	Michelman	high density polyethylene	40	129
W3	ML-160	Michelman	Carnauba	109	88
W4	ME77030	Michelman	paraffin/polyethylene	382	59 & 119 (2 Tm's)
W5	CC392-AS25	ChemCor	polyethylene	148	129
W6	CC325N35	ChemCor	high density polyethylene	54	131
W7	CC392N35	ChemCor	high density polyethylene	50	131
W8	CC Opacifier 341	ChemCor	ethylene-acrylic acid copolymer	79	99
W9	ME72040	Michelman	epolene-polyolefin resin	207	108
W10	ME02925	Michelman	polyethylene	45	95
W11	CC XL-21	ChemCor	polyethylene	509	115

Sample Preparation:

[0026] All samples were prepared by coating aqueous colloidal dispersions on the unexposed/processed (Dmin) Kodak Edge 5 Ektacolor paper at 3cc/sq.ft. with dryer temperature @ 140 °F to simulate tail-end of photofinishing process. Small amount of FT-248, an anionic fluorosurfactant available from Bayer AG, (used at 0.1% to 4% based on the total dry laydown of the layer, other surface active compounds can also be used) was used in the formulation to control the surface tension during coating.

Test for Water Resistance

[0027] Ponceau Red dye is known to stain gelatin through the ionic interaction. Ponceau red dye solution was prepared by dissolving 1 gram dye in 1000 grams mixture of acetic acid and water (5 parts: 95 parts). Samples were soaked in the dye solution for 5 minutes followed by a 30-second water rinse to removed excess dye solution on the coating surface, then air dried. A sample with good water resistant protective layer does not change the appearance by the test. A sample would showed very dense red color if there was no protective overcoat applied to the surface or the formulation did not form a continuous overcoat layer under the drying condition specified above to provide water resistance property.

Test for Durability on Wet Wiping

[0028] An approximately 1 inch-diameter water droplet was placed on the sample surface for 10 minutes. The excess water was then gently wiped up with a paper towel. This treated area was then rubbed with a dry paper towel for 40 passes under a pressure of 0.75 psi (500 grams over a 1.375 inch-diameter area). The scratches generated by the rubbing test were rated according to the description below. Higher ratings are more desirable.

Scratch Resistance Ratings:

[0029]

- 0 Totally abraded/worn
- 1 Dense scratches with associated haze band
- 2 Numerous scratches with associated haze band
- 3 Few scratches with associated haze band
- 4 Dense, heavy scratches
- 5 Numerous, heavy scratches
- 6 Few, heavy scratches
- 7 Dense, heavy scratches
- 8 Numerous, light scratches
- 9 Few, light scratches

10 No visible damage

Test for Dry Scratch Resistance

- 5 [0030] Each sample was rubbed with a dry paper towel for 40 passes under a pressure of 0.75 psi (500 grams over a 1.375 inch-diameter area). The scratches generated by the rubbing test were rated the same way as for wet wiping test described previously.

Test for Thermal Blocking

- 10 [0031] 3.5x4 sq. in. samples were preconditioned in 50%RH/60C for 2 hours, then placed face-to-face (the overcoat layer of one sample being in contact with the same overcoat of the other sample) in for 6 hours with 1000 grams weight placed on top of the samples. The samples were pulled apart and evaluated according to the following scale:

- 15 10 no adhesion, no tack
 9 very slight tack (aural observation)
 8 slight tack (aural observation)
 7 slight picking (visual observation)
 6 moderate picking
 20 5 significant picking
 4 0-25% coating removal
 3 25-50% coating removal
 2 50-75% coating removal
 1 100% coating removal (i.e. complete failure)

25 A ranking of 10 is most desirable, a ranking of 7 to 9 is also acceptable.

Gloss

- 30 [0032] Gloss measurement of samples was done on Gardner micro-tri-gloss meter, taking the average of five readings at 20-degree angle.

Coefficient of Friction

- 35 [0033] The kinetic coefficient of friction between a Carbide ball sled and the protective overcoat was measured and reported. All samples were condition in 70 °F/50%RH for at least 17 hours prior to the test.

Example 1

- 40 [0034] Sample No.1 was prepared with the protective overcoat consisting of P1 and P2 at 100 mg/sq.ft each. Sample No. 26 was prepared with the protective overcoat consisting of P2 and P3 at 100 mg/sq.ft. each. A series of samples similar to these two samples except the addition of wax particles in the protective overcoat formulation were prepared as described in Table 3. All samples showed superior water resistance property on Ponceau red dye staining test. The coefficient of friction of all samples containing wax particles were lower than that without wax particles (e.g. sample No. 1 and sample No.26) as expected. Also shown in Table 3 is the gloss of each sample, it is very apparent that when the particle size of wax particles exceeded 200 nm, the appearance of a print suffered from inferior gloss.

Table 3

50

Sample ID	Composition of protective layer	Comment	Particle size of wax particles (nm)	Coefficient of Friction	Gloss
1	see description above	comparison		0.668	71.4
2	as No.1 except add W1 @ 10mg/sq.ft.	Invention	50	0.516	71.4
3	as No.1 except add W1 @ 20 mg/sq.ft.	Invention	50	0.456	71.1

55

EP 0 915 373 A1

Table 3 (continued)

Sample ID	Composition of protective layer	Comment	Particle size of wax particles (nm)	Coefficient of Friction	Gloss
4	as No.1 except add W1 @ 30 mg/sq.ft.	Invention	50	0.427	71.1
5	as No.1 except add W1 @ 40 mg/sq.ft.	Invention	50	0.405	70.5
6	as No.1 except add W1 @ 50 mg/sq.ft.	Invention	50	0.388	70.1
7	as No.1 except add W1 @ 60 mg/sq.ft.	Invention	50	0.359	69.9
8	as No.1 except add W2 @ 10 mg/sq.ft.	Invention	40	0.544	70.1
9	as No.1 except add W2 @ 30 mg/sq.ft.	Invention	40	0.470	70.9
10	as No.1 except add W2 @ 50 mg/sq.ft.	Invention	40	0.499	72.4
11	as No.1 except add W3 @ 10 mg/sq.ft.	Invention	109	0.339	70.6
12	as No.1 except add W3 @ 30 mg/sq.ft.	Invention	109	0.268	68.9
13	as No.1 except add W3 @ 50 mg/sq.ft.	Invention	109	0.255	68.7
14	as No.1 except add W4 @ 10 mg/sq.ft.	comparison	382	0.341	67.9
15	as No.1 except add W4 @ 30 mg/sq.ft.	comparison	382	0.293	63.1
16	as No.1 except add W4 @ 50 mg/sq.ft.	comparison	382	0.273	56.8
17	as No.1 except add W5 @ 30 mg/sq.ft.	Invention	148	0.467	70.5
18	as No.1 except add W6 @ 30 mg/sq.ft.	Invention	54	0.488	71.7
19	as No.1 except add W7 @ 30 mg/sq.ft.	Invention	50	0.499	71.4
20	as No.1 except add W8 @ 30 mg/sq.ft.	Invention	79	0.405	69.2
21	as No.1 except add W9 @ 10 mg/sq.ft.	comparison	207	0.418	70.1
22	as No.1 except add W9 @ 30 mg/sq.ft.	comparison	207	0.358	67.3
23	as No.1 except add W9 @ 50 mg/sq.ft.	comparison	207	0.343	67.7
24	as No.1 except add W10 @ 10 mg/sq.ft.	Invention	45	0.441	70.9
25	as No.1 except add W11 @ 30 mg/sq.ft.	Invention	509	0.218	48.0

EP 0 915 373 A1

Table 3 (continued)

Sample ID	Composition of protective layer	Comment	Particle size of wax particles (nm)	Coefficient of Friction	Gloss
26	see description above	comparison		0.663	72.7
27	as No.26 except add W1 @ 30 mg/sq.ft.	Invention	50	0.330	70.1
28	as No.26 except add W2 @ 30 mg/sq.ft.	Invention	40	0.331	72.6
29	as No.26 except add W3 @ 30 mg/sq.ft.	Invention	109	0.237	69.3
30	as No.26 except add W4 @ 30 mg/sq.ft.	comparison	382	0.240	58.9
31	as No.26 except add W5 @ 30 mg/sq.ft.	Invention	148	0.353	70.4
32	as No.26 except add W6 @ 30 mg/sq.ft.	Invention	54	0.327	72.6
33	as No.26 except add W7 @ 30 mg/sq.ft.	Invention	50	0.325	72.3
34	as No.26 except add W8 @ 30 mg/sq.ft.	Invention	79	0.399	69.9
35	as No.26 except add W11 @ 30 mg/sq.ft.	comparison	509	0.327	70.0
36	as No.26 except add W10 @ 30 mg/sq.ft.	Invention	45	0.383	73.4

Example 2

[0035] Selected samples from Example 1 were tested for durability on wet wiping and dry scratches following the procedure described previously. The ratings of tested samples are shown in Table 4 below. As indicated by the higher ratings relative to the comparison sample without wax particles, the addition of wax particles in the protective layer formulation greatly improved the resistance of the print to scratches regardless of a wet sample or a dry sample. It is also noticed that a diminished improvement in scratch resistance was observed (e.g. sample No. 7) when the wax particles were used at higher than 20% by weight of the total laydown of the protective overcoat. It is reminded that samples containing W4, W9 or W11 also showed improvement in scratch resistance, however the gloss appearance was degraded badly as pointed out in Example 1.

Table 4

Sample ID	Composition of protective layer	Comment	dry scratch resistance	durability on wet wiping
1	see description above	comparison	5	4
2	as No.1 except add W1 @ 10 mg/sq.ft.	Invention	9	9
3	as No.1 except add W1 @ 20 mg/sq.ft.	Invention	10	9
4	as No.1 except add W1 @ 30 mg/sq.ft.	Invention	9	9
5	as No.1 except add W1 @ 40 mg/sq.ft.	Invention	5	9

EP 0 915 373 A1

Table 4 (continued)

Sample ID	Composition of protective layer	Comment	dry scratch resistance	durability on wet wiping
6	as No.1 except add W1 @ 50 mg/sq.ft.	Invention	6	5
7	as No.1 except add W1 @ 60 mg/sq.ft.	Invention	5	5
8	as No.1 except add W2 @ 10 mg/sq.ft.	Invention	8	8
9	as No.1 except add W2 @ 30 mg/sq.ft.	Invention	9	9
10	as No.1 except add W2 @ 50 mg/sq.ft.	Invention	6	5
12	as No.1 except add W3 @ 30 mg/sq.ft.	Invention	9	6
13	as No.1 except add W3 @ 50 mg/sq.ft.	Invention	9	6
14	as No.1 except add W4 @ 10 mg/sq.ft.	comparison	9	8
15	as No.1 except add W4 @ 30 mg/sq.ft.	comparison	9	9
16	as No.1 except add W4 @ 50 mg/sq.ft.	comparison	10	6
17	as No.1 except add W5 @ 30 mg/sq.ft.	Invention	8	9
18	as No.1 except add W6 @ 30 mg/sq.ft.	Invention	10	9
19	as No.1 except add W7 @ 30 mg/sq.ft.	Invention	8	9
20	as No.1 except add W8 @ 30 mg/sq.ft.	Invention	10	9
21	as No.1 except add W9 @ 10 mg/sq.ft.	comparison	9	8
22	as No.1 except add W9 @ 30 mg/sq.ft.	comparison	9	9
23	as No.1 except add W9 @ 50 mg/sq.ft.	comparison	9	5
24	as No.1 except add W10 @ 10 mg/sq.ft.	Invention	9	9
25	as No.1 except add W11 @ 30 mg/sq.ft..	Invention	9	9
26	see description above	Invention	9	8
30	as No.26 except add W4 @ 30 mg/sq.ft.	comparison	9	9
31	as No.26 except add W5 @ 30 mg/sq.ft.	Invention	9	9
32	as No.26 except add W6 @ 30 mg/sq.ft.	Invention	10	8

EP 0 915 373 A1

Table 4 (continued)

Sample ID	Composition of protective layer	Comment	dry scratch resistance	durability on wet wiping
33	as No.26 except add W7 @ 30 mg/sq.ft.	Invention	10	8
34	as No.26 except add W8 @ 30 mg/sq.ft.	Invention	10	7
35	as No.26 except add W11 @ 30 mg/sq.ft.	comparison	10	8

Example 3

[0036] Selected samples from Example 1 were tested for thermal blocking propensity following the procedure described previously. The ratings of tested samples are shown in Table 5 below. As indicated by the higher ratings compared to the comparison without wax particles, the addition of wax particles in the protective layer formulation significantly reduced the propensity of two prints to adhere to each other when being in contact face-to-face in high temperature environment. However, it is also indicated in Table 4 that the melting temperature of wax particle is preferred to be higher than 60 °C so as not to create a undesirable white mess on the surface of the print due to the melting of wax in high temperature environment. W4 consists of low melting component (59 °C) as well as a high melting component (119 °C), and apparently the low melting component (paraffin) melted during the test.

Table 5

Sample ID	Composition of protective layer	Comment	Melting temperature of wax particles (C)	Thermal Blocking (60C/50%RH/6 hrs)
1	see description above	comparison		4
2	as No.1 except add W1 @ 10 mg/sq.ft.	Invention	131	4
3	as No.1 except add W1 @ 20 mg/sq.ft.	Invention	131	5
4	as No.1 except add W1 @ 30 mg/sq.ft.	Invention	131	5
5	as No.1 except add W1 @ 40 mg/sq.ft.	Invention	131	5
6	as No.1 except add W1 @ 50 mg/sq.ft.	Invention	131	5
7	as No.1 except add W1 @ 60 mg/sq.ft.	Invention	131	6
11	as No.1 except add W3 @ 10 mg/sq.ft.	Invention	88	6
12	as No.1 except add W3 @ 30 mg/sq.ft.	Invention	88	7
13	as No.1 except add W3 @ 50 mg/sq.ft.	Invention	88	8
14	as No.1 except add W4 @ 10 mg/sq.ft.	comparison	59 & 119	wax melt on the surface
15	as No.1 except add W4 @ 30 mg/sq.ft.	comparison	59 & 119	wax melt on the surface
16	as No.1 except add W4 @ 50 mg/sq.ft.	comparison	59 & 119	wax melt on the surface

[0037] The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

1. An imaged photographic element having a protective overcoat thereon, the protective overcoat formed by the steps comprising;

providing an imaged photographic element having at least one silver halide light-sensitive emulsion layer;
applying an aqueous coating comprising a colloidal dispersion of a first polymeric particle having a glass transition temperature of greater than or equal to 25 °C and a particle size of from 5 to 500 nm and a second polymeric particle having a glass transition temperature of less than 25 °C and a particle size of from 5 to 500 nm and wax particles having a size of from 0.01 to 0.5 µm over the at least one silver halide light-sensitive emulsion layer wherein a weight ratio of the first polymeric particle to the second polymeric particle is from 3:97 to 80:20; and
drying the aqueous coating to provide an imaged photographic element having a protective overcoat.

2. The imaged photographic element having the protective overcoat of claim 1 wherein the aqueous coating has a solids concentration of from 1 to 50 percent.

3. The imaged photographic element having the protective overcoat of claim 1 wherein the first polymeric material comprises a polymer selected from the group consisting of polyesters, polyamides, polyurethanes, polyureas, polyethers, polycarbonates, polyacid anhydrides and addition polymers.

4. The imaged photographic element having the protective overcoat of claim 1 wherein the second polymeric material comprises a polymer selected from the group consisting of polyesters, polyamides, polyurethanes, polyureas, polyethers, polycarbonates, polyacid anhydrides and addition polymers.

5. The imaged photographic element having the protective overcoat of claim 1 wherein the aqueous coating further comprises biocides, surfactants and lubricants.

6. The imaged photographic element having the protective overcoat of claim 1 wherein the wax particles comprise a material selected from the group consisting of polypropylenes, polyethylenes, microcrystalline waxes, paraffin and natural waxes.

7. The imaged photographic element having the protective overcoat of claim 1 wherein the size of the wax particles is from 0.01 µm to 0.2 µm.

8. The imaged photographic element having the protective overcoat of claim 1 wherein the wax particles have a melting point of greater than 60°C.

9. An imaged photographic element comprising:

a support;
at least one silver halide light-sensitive emulsion layer superposed on the support; and
protective overcoat furthest from the support superposed on the at least one silver halide light sensitive layer comprising a first polymeric particle having a glass transition temperature of greater than or equal to 25 °C and a particle size of from 5 to 500 nm and a second polymeric particle having a glass transition temperature of less than 25 °C and a particle size of from 5 to 500 nm at a weight ratio of the first polymeric particle to the second polymeric particle of from 3:97 to 80:20 and wax particles having a size of from 0.01 µm to 0.5 µm.

10. The imaged photographic element having the protective overcoat of claim 9 wherein the first polymeric material comprises a polymer selected from the group consisting of polyesters, polyamides, polyurethanes, polyureas, polyethers, polycarbonates, polyacid anhydrides and addition polymers.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 3595

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	US 5 643 972 A (WANG ET AL.) 1 July 1997 * column 2, line 9 - line 14 * * column 2, line 33 - line 39 * * column 3, line 15 - line 21 * * column 5, line 34 - line 44 * * column 5, line 66 - column 6, line 1 * * column 6; table 1 * * column 7; table 2 *	1-10	G03C1/76 G03C11/08
Y	US 5 529 891 A (WANG ET AL.) 25 June 1996 * column 1, line 65 - column 2, line 15 * * column 2, line 41 - line 44 * * column 3, line 13 - line 15 * * column 5, line 12 - line 18 * * column 5, line 25 - line 30 * * table 1 *	1-10	
Y	GB 482 204 A (I.G.FARBENINDUSTRIE) * page 1, line 75 - line 82; claim 1 *	1-10	
A	US 5 376 434 A (OGAWA ET AL.) 27 December 1994 * column 2, line 67 - column 3, line 32 * * column 3, line 37 - line 43 * * column 4, line 3 - line 9 * * column 7, line 56 - column 8, line 17 * * column 10, line 22 - line 40 *	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 December 1998	Examiner Magrizos, S
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons A: member of the same patent family, corresponding document	

EPO FORM 1503 03/92 (P/4C01)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 98 20 3595

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-12-1998

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5643972 A	01-07-1997	US 5447832 A EP 0675401 A JP 8050344 A	05-09-1995 04-10-1995 20-02-1996
US 5529891 A	25-06-1996	EP 0745895 A JP 8314067 A	04-12-1996 29-11-1996
GB 482204 A		NONE	
US 5376434 A	27-12-1994	JP 6110169 A	22-04-1994

DOCKET NO: 1999P 2416
 SERIAL NO: _____
 APPLICANT: Harold Frank et al.

LERNER AND GREENBERG P.A.
 P.O. BOX 2480
 HOLLYWOOD, FLORIDA 33022
 TEL. (954) 925-1100